DaimlerChrysler AG

Exhaust gas cleaning system for an internal combustion engine

The invention concerns an exhaust gas catalyst system for an internal combustion engine with at least one catalytically active component according to the preamble of patent claim 1.

Catalytic converters ordinarily have a relatively restricted optimal thermal functioning range for ensuring proper cleaning of exhaust gas which in the case of NOx storage catalytic converters for example is between 190°C and 500° C. Below this range, they are not yet sufficiently catalytically active to be fully functional and to store the undesired pollutants contained in the exhaust gas and/or convert them into harmless substances, while above this range, a very strong deactivation associated with a strong thermal aging occurs and finally a destruction of the catalytic converter as a result of overheating. Since the temperature of the catalytic converter essentially is determined by the temperature of the exhaust gases flowing through it, control, in particular limiting, of the exhaust gas temperature through mechanical means and/or targeted cooling of exhaust gas is therefore of special importance for the proper operation of exhaust gas catalytic converters. No less important, however, is also the thermic behavior of the exhaust gas catalytic converters themselves, e.g., good temperature resistance in ranges of relatively high exhaust gas temperatures or good light-off performance in order to be able to quickly reach their full catalytic activity so that efficient cleaning of exhaust gas is ensured.

A method for the treatment of exhaust gases of a diesel engine for the reduction of particle emissions is known from DE 197 18 727 C2, in which the diesel exhaust gas is directed through two diesel catalytic converters arranged one behind the other, with the cell density of the downstream, second catalytic converter being greater than that of the first catalytic converter.

The object of the invention is to provide an exhaust gas cleaning system for an internal combustion engine, preferably for a diesel engine, in which reaction heat conversion is distributed uniformly over the entire length of the catalytically active components and aging behavior is improved.

The invention achieves this object by providing an exhaust gas cleaning system with the features of claim 1. In this exhaust gas cleaning system, the exhaust-gas-side surface of the catalytically active coating in the intake region of the catalytically active components has at least partially a diffusion layer or is at least partially covered by a diffusion layer.

In a refinement of the exhaust gas cleaning system according to claim 2, the at least one region with high light-off temperature in combination with high temperature resistance in contrast to the at least one other region with a low light-off temperature in combination with a reduced temperature resistance in comparison to the at least one region has a lower specific noble metal content and/or a larger noble metal particle diameter.

In an advantageous embodiment according to claim 3, the cell density in the intake region (higher and/or intermediate temperature region) of the catalytically active component is lower than in the discharge region (lower temperature region) of the catalytically active component.

According to claim 4, the catalytically active component is configured in its intake region with a support material with higher specific heat capacity and in its discharge region with a support material with lower specific heat capacity. As a result, a deactivation of the catalytic converter induced by a hot spot can be suppressed in a most advantageous manner and at the same time good light-off behavior can be achieved. For example, ceramic or ceramic-containing materials and/or metals or metal-containing materials as well as other materials suited to the particular application purpose can advantageously be used as supporting materials with differing specific heat capacity.

In an alternative refinement of the invention according to claim 5, the catalytically active component has a cone shape.

Furthermore, in a refinement of the invention according to claim 6, the catalytically active coating is in multiple layers, with the individual layers having differing composition. The at least one region with high light-off temperature in combination with a high temperature resistance is oriented toward the exhaust gas side and the at least one additional region with a low light-off temperature in combination with reduced temperature resistance in comparison with the at least one region is applied to the side oriented away from the exhaust gas. The start-up temperature of a catalytically active component is referred to as light-off temperature.

In a preferred embodiment of the invention according to claim 7, the catalytically active coating with at least one region of high light-off temperature and with at least one further region with a low light-off temperature is applied in the form of a gradient, with the high light-off temperature being applied predominantly in the intake region of the catalytically active component and predominantly the at least one other region with a lower light-off temperature being applied in the discharge region of the catalytically active component.

In a further preferred embodiment according to claim 8, the catalytically active coating has predominantly or wholly the at least one further region with a low light-off temperature in combination with reduced temperature resistance.

The catalytically active component can, for example, be configured as an oxidation catalytic converter, an NO_x storage catalytic converter, an SCR catalytic converter and/or as a particle filter.

Advantageous embodiments of the exhaust gas cleaning system according to the invention are the object of the subclaims and the description.

Furthermore, advantageous embodiments of the invention are presented in the drawings and are described below, wherein by way of example:

FIG 1 shows a schematic depiction of a first embodiment of the invention

FIG 2 shows a schematic depiction of a second embodiment of the invention

FIG 3 shows a schematic depiction of a third embodiment of the invention

FIG 4 shows a conversion behavior of an NO_x storage catalytic converter according to the state of the art

FIG 5 shows an optimized conversion behavior of an NO_x storage catalytic converter according to the invention.

The schematic depiction of FIG 1 shows an arrangement of a catalytically active coating 1 using the example of an NO_x storage catalytic converter. Exhaust gas catalytic converters ordinarily comprise a support material or a support body 6 with catalytically active coating 1 applied thereto, which for example can be applied to the support body by means of a porous washcoat of Al_2O_3, SiO_2, TiO_2, ZrO_2, zeolites and/or mixtures thereof together with activity enhancing additives or promoters. Frequently serving as support body for catalytic converters are ceramic catalytic converters with a honeycomb-like structures, preferably of cordierite or other suitable materials. Alternatively, however, support bodies of metal can also be used. Furthermore, the catalytically active component can be configured in its intake region with a support material with higher specific heat capacity and with a support material with lower specific heat capacity in its discharge region so that materials such as, for example, metal or metal-containing materials and ceramic or ceramic-containing material can be jointly utilized as support material or support body for a catalytic component. As depicted in FIG 1, the catalytically

active coating 1 of the NO_x storage catalytic converter is constructed of individual layers of differing composition. The at least one region with high light-off temperature in combination with a high temperature resistance 2 is directed toward the exhaust side and the at least one other region with a low light-off temperature in combination with a reduced temperature resistance 3 in comparison with the at least one region being applied to the side directed away from the exhaust gas. Region 2 thus is characterized in comparison with region 3 by a poorer low-temperature activity, but a higher high-temperature resistance, while region 3 in contrast has an opposed behavior and is responsible for good overall conversion and good cold-start behavior. Through the incorporation of region 2 in the intake region of the catalytically active component, the activity in the lower and/or intermediate temperature range is reduced.

Regions 2 and 3 contain platinum-group metals, in particular platinum and/or rhodium, as catalytic converter material, as well as alkali or earth alkali metals, which are characterized by their storage capacity for oxides of nitrogen. This property is utilized in NO_x storage or adsorber catalytic converters. Under lean operating conditions ($\lambda>1$), the nitric oxides are converted as follows:

$$2NO + O_2 \rightarrow 2NO_2 \text{ (Pt catalytic converter)}$$
$$4NO_2 + O_2 + 2BaCO_3 \rightarrow 2Ba(NO_3)_2 + 2CO_2$$

Under rich exhaust gas conditions ($\lambda<1$), nitrogen dioxide is desorbed back out of the storage and is converted directly with the carbon monoxide present in the exhaust gas into nitric oxide:

$$2Ba(NO_3)_2 + 2CO_2) \rightarrow 4NO_2 + O_2 + 2BaCO_3$$
$$2NO_2 + 4CO \rightarrow 4CO_2 + N_2 \text{ (Pt, Rh catalyzed)}$$

The switch-over times between lean and rich operation of the engine depend on the quantity of storage material used, the NO_x emissions and the parameters typical for all catalyzed reactions such as gas throughput and temperature.

Furthermore, regions 2 and/or 3 can include oxygen storage components such as a cerium compound, with the most important substance being the cerium oxide. Oxygen storage components equalize the air ratio fluctuations in λ-1 regulated engines since they can change their oxidation state from +III to +IV and vice versa:

$2CeO_2 + CO \rightarrow Ce_2O_3 + CO_2 \rightarrow (\lambda<1)$

$2Ce_2O_3 + O_2 \rightarrow 4CeO_2 \rightarrow (\lambda>1)$

By this means, a constant air ratio is obtained. In addition, cerium supports the noble metal dispersion.

In order to control the temperature resistance of catalytic converter coatings, compounds of the elements La, Zr, etc., preferably as oxides, can also be contained.

The choice of the composition of regions 2, 3, in particular the concentration of noble metal in combination with the noble metal diameter is closely bound with the particular exhaust gas temperature window to which respective regions 2, 3 are exposed. As a result, the catalytic activity of the regions can be controlled alongside other measures. Through a lower concentration of noble metal and/or a larger particle size it is possible first to avoid excessively large conversion immediately after intake into the catalytic converter, by which means an excessively high temperature and loads on the intake side of the catalytic converter can be avoided. Second, it can be provided through the selection of a relatively large concentration of noble metal and of a relatively small particle size that in the downstream region the required activity for conversion of the pollutants is present in sufficient degree or can even be increased.

Furthermore, the exhaust-gas-side surface of catalytically active coating 1 in the intake region of the NOx storage catalytic converter at least partially has a diffusion layer 4 or is at least partially covered by a diffusion layer 4. The diffusion layer itself essentially contains oxides of aluminum, cerium and/or zirconium and causes a kinetic retardation of the chemical reactions proceeding at this location, in particular transport or diffusion processes. By this means

temperature peaks, so-called hot spots, are advantageously suppressed in the catalytic converter intake region and the thermal load in the intake region is reduced without in so doing impairing the cold start behavior of the system.

The manufacture of catalytic converters is well documented in the literature in terms of the general procedure.

By variation of the cell densities (in the intake region of the catalytic converter lower cell densities, for example 200 to 400 cpsi, and in the discharge region of the catalytic converter higher cell densities, for example 600 to 900 cpsi) and the use of conical catalytic converter structures (a narrower catalytic converter diameter in the intake region and an increasing diameter in the discharge region), the sojourn time for the exhaust gas in the different catalytic converter regions can be controlled, i.e., in the intake area high flow speeds prevail while in the back region a longer sojourn time of the exhaust gas and thus a greater conversion plays a role.

FIG 2 shows by way of example in schematic representation a variant according to the invention of a catalytically active coating 1 using the example of a NO_x storage catalytic converter, with for the sake of simplicity the same reference characters being used for the same components or components achieving the same function and to this extent reference can be made to the above description for FIG 1. In other respects, the advantages mentioned in FIG 1 and in the general part of the description likewise apply for the embodiment according to the invention in FIG 2 and for all subsequently mentioned embodiment forms. The exhaust gas aftertreatment apparatus of FIG 2 includes a catalytically active coating 1 with at least one region with high light-off temperature in connection with a high temperature resistance 2 and with at least one other region with a low light-off temperature in combination with a reduced temperature resistance 3 in comparison with the at least one region. The region 5, comprising the regions 2 and/or 3, are [sic] applied in the manner of a gradient to the catalytic converter support, within intake area E of the catalytic converter predominantly the region with high light-off temperature 2 being applied and in discharge area A of the catalytic converter

predominately the at least one other region with a low light-off temperature 3 being applied. The exhaust-gas-side surface of the catalytically active coating 1 in the intake region of the NO_x storage catalytic converter likewise has at least partially a diffusion layer 4 or is at least partially covered by a diffusion layer 4.

FIG 3 shows in a schematic representation by way of example a further variant according to the invention of a catalytically active coating 1 using the example of an NO_x storage catalytic converter, in the case of which region 3 is provided on the catalytic converter support. The exhaust-gas-side surface of the catalytically active coating 1 in the intake region of the NO_x storage catalytic converter in like manner has here also at least one diffusion layer 4 or is at least partially covered by a diffusion layer 4.

In FIG 4, the total conversion of the NO_x storage catalytic converter is plotted as a function of the catalytic converter length. The steep rise of the curve at the beginning clearly shows the high activity of the catalytic converter and the associated high exothermy of the reaction in its intake region. This leads to a premature aging or even damage in the intake region of the catalytic converter.

FIG 5 in contrast demonstrates an optimized conversion behavior, which is retained with all embodiment forms according to the invention, with it being possible to utilize the recommended measures for optimization of conversion individually or in combination. Through the invention, the conversion and above all the associated exothermy, i.e. the quantities of heat released in the catalytic reaction advantageously are distributed more uniformly on the entire NO_x storage catalytic converter. The thermic load of the first region of the catalytic converter region is thereby reduced without the cold-start behavior of the system being thereby impaired. In addition, temperature peaks in the intake region are thus effectively avoided.